Electronic Supplementary Information

Isotropic rotation in amphidynamic crystals of stacked carbazole-based rotors featuring halogen-bonded stators.

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Materials and methods

All reagents were purchased from Sigma-Aldrich and used as received. The THF was dried prior to use by distillation over Na/benzophenone. Flash column chromatography was performed using Aldrich silica gel 230-400 mesh. Reactions were monitored by TLC on silica gel plates 60 F254 (Merck) and spots were detected either by UV-absorption or by using the Seebach’s TLC stain. $^1$H and $^{13}$C NMR data for all previously compounds were recorded at ambient temperature using Bruker Fourier300, Jeol Eclipse 300 and Bruker AV500 with cryoprobe spectrometers and are referenced to THF (1.73 ppm, 25.2 ppm) or CDCl$_3$ (7.26 ppm, 77.0 ppm), as indicated. The FT-IR spectral data were recorded with Bruker ATR in the 450-4000 cm$^{-1}$ range. Melting points were determined using Fisher Johns melting point apparatus (uncorrected) or by Differential Scanning Calorimetry. HRMS were obtained by Direct Analysis in Real Time (DART) in AccuTOF, JMS-T100LC.
1,4-bis(3,6-dibromo-9H-carbazol-9-yl)benzene (1)

In a round-bottom flask were dissolved 0.500 g of 4 (1 eq, 1.23 mmol) and 0.961 g of N-bromosuccinimide (4.4 eq, 5.39 mmol) in 4 mL of anhydrous N,N'-dimethylformamide. The mixture was refluxed under nitrogen atmosphere for 4 h. After that time, the crude was poured into water (30 mL) and a light brown solid was filtered and washed with water. Subsequently, the obtained solid was washed with dichloromethane-ethanol and recrystallized from THF to give a white solid (0.751 g, yield 85%, m.p. by DSC 400.3-404.0 °C). $^1$H NMR (500 MHz, THF-$d_8$) δ: 8.44 (d, $J= 2.0$ Hz, 4H), 7.92 (s, 4H), 7.60 (dd, $J= 9.0$, 2.0 Hz, 4H), 7.51 (d, $J= 9.0$ Hz, 4H). $^{13}$C NMR (125 MHz, THF-$d_8$) δ: 140.6 (C-10), 137.2 (C-13), 130.2 (C-4), 129.4 (C-14), 125.2 (C-11), 124.4 (C-2), 114.1 (C-3), 112.4 (C-1). IR (ATR, cm$^{-1}$) ν= 3053, 1514, 1466, 1428, 1224, 1059, 795. HRMS (DART) C$_{30}$H$_{17}$Br$_4$N$_2$ m/z calc. 724.80843, found 724.80977, difference 1.85 ppm.

1,4-bis(3,6-dibromo-9H-carbazol-9-yl)benzene-d4 (1-d$_4$)
The same procedure employed for 1 was used to prepare the deuterated compound 1-d₄ with the following quantities: 0.500 g of 4-d₄ (1 eq, 1.21 mmol) and 0.952 g of N-bromosuccinimide (4.4 eq, 5.33 mmol) in 4 mL of anhydrous N,N'-dimethylformamide. The product was recrystallized from THF as a white solid (0.722 g, yield 82%), m.p. >250ºC. ¹H NMR (500 MHz, THF-d₈) δ: 8.44 (d= 2.0 Hz, 4H), 7.60 (dd, J= 9.0, 2.0 Hz, 4H), 7.51 (d, J= 9.0 Hz, 4H). ¹³C NMR (125 MHz, THF-d₈) δ: 140.6 (C-10), 130.2 (C-4), 125.2 (C-11), 124.4 (C-2), 114.1 (C-3), 112.4 (C-1). IR (ATR, cm⁻¹) ν= 3055, 1468, 1441, 1221, 1058, 1019, 798. HRMS (DART) C₃₀H₁₃D₄Br₄N₂ m/z calc. 728.83354, found 728.83375 difference 0.29 ppm.

1,4-bis(3,6-dichloro-9H-carbazol-9-yl)benzene (2)

In a round-bottom flask were dissolved 0.500 g of 4 (1 eq, 1.23 mmol) and 0.721 g of N-chlorosuccinimide (4.4 eq, 5.41 mmol) in 4 mL of anhydrous N,N-dimethylformamide. The mixture was refluxed under nitrogen atmosphere for 4 h. After that time, the crude was poured into water (30 mL) and the solid was filtered and washed with water. Next, the solid was washed with dichloromethane-ethanol and recrystallized from THF to give a white solid (0.493 g, yield 73%, m.p. by DSC 384.7-391.2 ºC). ¹H NMR (500 MHz, THF-d₈) δ: 8.28 (d, J= 2.0 Hz, 4H), 7.93 (s, 4H), 7.56 (d, J= 9.0 Hz, 4H), 7.47 (dd, J= 9.0, 2.0 Hz, 4H). ¹³C NMR (125 MHz, THF-d₈) δ: 140.5 (C-10), 137.2 (C-13), 129.4 (C-14), 127.5 (C-4), 126.8 (C-3), 124.8 (C-11), 121.3 (C-2), 112.0 (C-1). IR (ATR, cm⁻¹) ν= 3057, 1513, 1468, 1432, 1345, 1314, 1273, 1223, 1079, 1067, 797. HRMS (DART) C₃₀H₁₇Cl₄N₂ m/z calc. 547.01163, found 547.01212 difference 0.49 ppm.
1,4-bis(3,6-diiodo-9H-carbazol-9-yl)benzene (3)

In a three-neck round-bottom flask were dissolved 0.100 g of 4 (1 eq, 0.246 mmol), 0.199 g of potassium iodide (5 eq, 1.23 mmol) and 0.312 g of potassium iodate (6 eq, 1.456 mmol) in 10 mL of glacial acetic acid. The mixture was stirred and heated to 80 ºC under nitrogen atmosphere for 10 h. Afterwards, the crude was poured into 30 mL of an aqueous saturated solution of Na$_2$SO$_3$ where the desired compound precipitated as a yellow solid. This solid was filtered and washed three times with water. Finally, the solid was recrystallized from THF to give a white solid (0.167 g, 75%, m.p. determinated by DSC 415.7 ºC). $^1$H NMR (500 MHz, THF-$d_8$) δ: 8.61 (d, $J$= 2 Hz, 4H), 7.90 (s, 4H), 7.75 (dd, $J$= 9 Hz, 2 Hz, 4H), 7.39 (d, $J$= 9 Hz, 4H). $^{13}$C NMR (125 MHz, THF-$d_8$) δ: 140.8 (C-10), 137.0 (C-13), 135.7 (C-2), 130.5 (C-4), 129.3 (C-14), 125.5 (C-11), 112.7 (C-1), 83.8 (C-3). IR (ATR, cm$^{-1}$) ν= 3401, 3053, 1515, 1226, 1054, 795, 453. HRMS (DART) C$_{30}$H$_{17}$I$_4$N$_2$ m/z calc. 912.76767, found 912.75704 difference 11.64 ppm.

1,4-bis(3,6-diiodo-9H-carbazol-9-yl)benzene-d$_4$ (3-d$_4$)

The same experimental procedure as in the previous compound 3 was used, with the following quantities: 0.100 g of 4-d$_4$ (1 eq, 0.242 mmol), 0.201 g of potassium iodide (5 eq, 1.21 mmol); 0.311 g of potassium iodate (6 eq, 1.452 mmol) were dissolved in 10 mL of
glacial acetic acid. The isolated product was a white solid (0.162 g, 73%). $^1$H NMR (500 MHz, THF-$d_8$) $\delta$: 8.61 (d, $J= 2$ Hz, 4H), 7.75 (dd, $J= 8$ Hz, 2 Hz, 4H), 7.39 (d, $J= 8$ Hz, 4H). $^{13}$C NMR (125 MHz, THF-$d_8$) $\delta$: 140.8 (C-10), 136.9 (C-13), 135.8 (C-2), 130.5 (C-4), 125.5 (C-11), 112.7 (C-1), 83.8 (C-3). IR (ATR, cm$^{-1}$) $\nu$: 3395, 3071, 1594, 1473, 1442, 1227, 1050, 800, 453. HRMS (DART) C$_{30}$H$_{13}$D$_{4}$I$_{4}$N$_{2}$ m/z calc. 916.78215, found 916.77827 difference 4.24 ppm.

1,4-di(9H-carbazol-9-yl)benzene (4)

\[
\begin{align*}
\text{(1)苯} & \quad \text{CuI} \\
\text{18-crown-6} & \quad K_2CO_3 \\
\text{DMPU} & \quad 140 \degree C
\end{align*}
\]

In a three-neck round-bottom flask were added 0.500 g of carbazole (2 eq, 3 mmol), 0.491 g of 1,4-diiodobenzene (1 eq, 1.50 mmol), 0.028 g of CuI (0.1 eq, 0.15 mmol), 0.013 g of 18-crown-6 (0.02 eq, 0.03 mmol) and 0.831 g of K$_2$CO$_3$ (4 eq, 6 mmol) and 4 mL of N,N-dimethylpropylene urea and heated to 140 ºC for 1.5 h under nitrogen atmosphere. The crude was poured into 30 mL of an aqueous saturated solution of NH$_4$Cl. The solid was filtrated and washed with water. Finally, the solid was recrystallized from dichloromethane-acetonitrile to give a white solid (0.481 g, yield 80%, m.p. by DSC 322-324 ºC). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 8.2 (d, $J= 8.0$ Hz, 4H), 7.8 (s, 4H), 7.58 (d, $J= 8.0$ Hz, 4H), 7.5 (ddd, $J= 8.0, 7.0, 1.0$ Hz, 4H), 7.36 (ddd, $J= 8.0, 7.0, 1.0$ Hz, 4H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 140.8 (C-10), 136.7 (C-13), 128.4 (C-14), 126.2 (C-2), 123.6 (C-11), 120.5 (C-4), 120.3 (C-3), 109.8 (C-1). IR (ATR, cm$^{-1}$) $\nu$: 3051, 1513, 1445, 1311, 1225, 748, 720. HRMS (DART) C$_{30}$H$_{21}$N$_{2}$ m/z calc. 409.17047, found 409.17038.
1,4-di(9H-carbazol-9-yl)benzene-\textsubscript{d\textsubscript{4}} (4-\textsubscript{d\textsubscript{4}})

The same procedure for the synthesis of compound 4 was used with the following quantities: 0.500 g of carbazole (2 eq, 3 mmol), 0.461 g of 1,4-diiodobenzene-\textsubscript{d\textsubscript{4}} (1 eq, 1.50 mmol), 0.028 g of Cul (0.1 eq, 0.15 mmol), 0.013 g of 18-crown-6 (0.02 eq, 0.03 mmol) and 0.831 g of K\textsubscript{2}CO\textsubscript{3} (4 eq, 6 mmol) and 4 mL of N,N-dimethylpropylene urea, heated to 140 °C for 1.5 h under nitrogen atmosphere. The product was isolated as a beige solid (0.423 g, yield 75%). \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\): 8.16 (dd, \(J= 8.0, 1.0\) Hz, 4H), 7.54-7.52 (m, 4H), 7.48-7.42 (m, 4H), 7.31 (ddd, \(J=8.0, 7.0, 1.0\) Hz, 4H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\): 140.9 (C-10), 136.7 (C-13), 128.0 (C-14), 126.1 (C-2), 123.7 (C-11), 120.5 (C-4), 120.3 (C-3), 109.8 (C-1). (IR (ATR, cm\textsuperscript{-1}) \(\nu\)= 3050, 1493, 1446, 1333, 1310, 1226, 749, 721. HRMS (DART) C\textsubscript{30}H\textsubscript{17}D\textsubscript{4}N\textsubscript{2} m/z calc. 413.19558, found 413.19551 difference 0.18 ppm.

**X-Ray diffraction studies**

Data collection were performed at 296 K and 150 K on a Bruker-APEX-II CCD diffractometer with Mo K\textsubscript{α}-radiation, \(\lambda = 0.71073\) Å or Bruker-D8-Venture diffractometer with Cu K\textsubscript{α}-radiation, \(\lambda = 1.54178\) Å. The structures were solved by direct methods and refined using SHELXXL-2014. All non-hydrogen atoms were refined anisotropically.
**Figure S 1.** Compound 1  a) Unit cell  b) ORTEP diagram at 296 K  c) ORTEP diagram at 150 K, both with thermal ellipsoids at 35% probability.

**Figure S 2.** Different perspectives of the halogen bonds (Br-Br) in the crystal packing of compound 1  a) View down the c axis b) View down the b axis
**Figure S 3.** Compound 4 a) Unit cell b) ORTEP diagram at 298 K with thermal ellipsoides at 35% probability c) Packing view from b axis with CH-C interaction
Figure S 4. Crystal structures of 1 at different temperatures from 180 K to 270 K
Table S1. Comparison of relevant crystallographic parameters of compounds 1 (variable temperature) and 4

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*a=Crystallographic information from Aguilar-Granda A. et.al. DOI: 10.1021/acs.cgd.6b00395*
X-Ray powder diffraction

Analyses were carried out using Cu-Kα = 1.5406 Å radiation, data were collected at room temperature in the range of 2Θ= 5-50° (step of 0.017°, step time 40.005 s), comparison can be seen in Figures S5 and S6.

**Figure S 5.** Comparison of powder X-ray diffraction patterns. (a) Calculated from crystalline structure of compound 1. (b), (c) and (d) Experimental patterns from compounds 1, 2 and 3, respectively

**Figure S 6.** Comparison of powder X-ray diffraction patterns. (a) Calculated from crystalline structure of compound 1. (b) and (c) Experimental patterns from compounds 1-d4, 2-d4 and 3-d4, respectively.
Thermal analyses

Compounds 1 and 2: Differential scanning calorimetry was carried out on a DSC analyzer under nitrogen atmosphere, using a heating cycle from 25 to 550 °C with a heating rate of 10 °C/min. Thermogravimetric analyses were obtained on a thermoanalyzer under argon atmosphere using a temperature interval from 30 to 550 °C with a heating rate of 10 °C/min. For the compound 3: Differential scanning calorimetry and thermogravimetric analyses were carried out on a DSC analyzer Netzsch STA 449 F3 Jupiter under nitrogen atmosphere from 25 to 550 °C with a heating rate of 10 °C/min.

Figure S 7. Differential scanning calorimetry of compound 1 from 173 K to 573 K
Figure S 8. Thermal analyses of compound 1 (top) Differential scanning calorimetry (DSC); (bottom) Thermogravimetric analyses (TG).
Figure S 10. Thermal analyses of compound 3 (top) Differential scanning calorimetry (DSC); (bottom) thermogravimetric analyses (TG)
Solid state $^2$H NMR

Solid state $^2$H NMR experiments were carried out on a Bruker AV300 spectrometer operating at a frequency of 46.07 MHz, using a 4 mm wide-line probe with a $2/\pi$ pulse of 2.5 µs and recycle delay of 20 s. The spectra were acquired by averaging at least 256 scans and processed with a line broadening of 2 kHz. The sample was placed inside a borosilicate glass NMR tube between two glass rods. The temperature inside the probe was calibrated by using the shift of $^{207}$Pb as the reference.

**Figure S 16.** Solid state $^2$H NMR spin-echo experiment of compounds 1 (top), 3 (middle) and 4 (bottom) all at room temperature
Figure S 17. Variable temperature $^2$H NMR using the spin echo technique for compound 1
**Deuterium simulations**

The $^2$H NMR line shapes were simulated using the NMRWebLab 6.0.4; in all cases a Quadrupolar Coupling Constant (QCC) of 176 KHz was employed. The line shapes from 333 K to 246 K (*Superfast dynamics*) were simulated using 2-fold jumps (angular displacement of 180º) in the fast exchange regime and a cone angle (θ) of 54.7º. On the other hand, the line shapes from 206 K to 145 K (*Initial Dynamics*) were simulated using a 2-fold motion model in the fast regime with phenylene libration of 70º and a cone angle (θ) of 60º. Finally, the intermediate traces were successfully simulated using a ratio with the superfast/initial dynamics. In these cases, relative proportions of 95:5 (236 K), 80:20 (226 K) and 25:75 (216 K) were obtained.

![Figure S 18. Comparison between experimental (solid line) and simulated (dashed line) $^2$H NMR line shapes of compound 1 at the indicated temperatures.](image)

S18
Proton spin lattice relaxation experiments ($^1\text{H} T_1$, NMR).

$^1\text{H} T_1$ measurements were carried out using a commercial magnet set at a magnetic field strength $B_0$ of 1.03 T, at which the proton frequency ($\nu_0 = \omega_0/2\pi$) is 44.1 MHz. A tank circuit was built for this purpose using an inductor made of bare copper wire wound in a coil form. A polycrystalline sample of compound 1 was packed in a borosilicate glass tube (5 mm diameter, 1.0 cm length) caped with Teflon tape plugs and placed in the copper coil. $^1\text{H} T_1$ experiments were recorded using a saturation recovery pulse sequence combined with a spin-echo, the saturation state was attained with a pulse comb (X*p/2) which was followed by a time recovery $\tau$. Saturation recovery traces were fitted to a single exponential function. $^1\text{H} T_1$ experiments were recorded in the range of 50 K – 190 K.

![Graph](image)

**Figure S 19.** Representative example of a $^1\text{H}$ spin lattice relaxation experiment at 65K recorded at a frequency of 44.1MHz using the saturation recovery pulse sequence. The delay times (tau) employed were 100 ms, 160 ms, 250 ms, 400 ms, 600 ms, 1 s, 1.6 s, 2.5 s, 4 s, 6 s, 10 s, 16 s, 25 s, 40 s, 60s, 80 s. The data were fitted to a single exponential and the calculated $T1$ was found to be 12.2 s.
Figure S 20. Spectra of a representative $^1H$ T$^1$ NMR experiment performed at 65 K at 44.1 MHz frequency for proton. The spectra display different intensities obtained with the following tau delay times: 100 ms, 160 ms, 250 ms, 400 ms, 600 ms, 1 s, 1.6 s, 2.5 s, 4 s, 6 s, 10 s, 16 s, 25 s, 40 s, 60 s, 80 s.
Solution NMR spectroscopic analyses

**Figure S25.** $^1$H NMR spectrum of 4 (300 MHz, CDCl$_3$)
Figure S 11. $^1$H NMR spectrum of $6$ (300 MHz, CDCl$_3$)

Figure S 26. $^{13}$C NMR spectrum of $4$ (75 MHz, CDCl$_3$)
Figure S27. $^1$H NMR spectrum of 4-d$_4$ (300 MHz, CDCl$_3$)
Figure S 28. $^{13}$C NMR spectrum of 4-$d_4$ (75 MHz, CDCl$_3$)
Figure S 29. $^1H$ NMR spectrum of I (500 MHz, THF-$d_8$)
Figure S 30. $^{13}$C NMR spectrum of 1 (125 MHz, THF-d$_8$)
Figure S 31. $^1$H NMR spectrum of 1-\(\text{d}_4\) (500 MHz, THF-\(\text{d}_8\))
Figure S 32. $^{13}C$ NMR spectrum of 1-$d_4$ (125 MHz, THF-$d_8$)
Figure S 33. $^1$H NMR spectrum of 2 (500 MHz, THF-$d_8$)
Figure S 34. $^{13}$C NMR spectrum of 2 (125 MHz, THF-$d_8$)
Figure S 35. $^1$H NMR spectrum of 3 (500 MHz, THF-$d_8$)
Figure S 36. $^{13}$C NMR spectrum of 3 (125 MHz, THF-$d_8$)
**Figure S 37.** $^1H$ NMR spectrum of 3-$d_4$ (500 MHz, THF-$d_8$)
Figure S 38. $^{13}$C NMR spectrum of 3-$d_4$ (125 MHz, THF-$d_8$)